USE OF AN OPTICAL METHOD TO ORIENT BENZENE CRYSTALS

FRANK A. MULLENS

USE OF AN OPTICAL METHOD TO ORIENT BENZENE CRYSTALS

by

Frank A. Mullens
//
Captain, United States Army

Submitted in partial fulfillment of
the requirements for the degree of

MASTER OF SCIENCE
IN
PHYSICS

United States Naval Postgraduate School
Monterey, California

1 9 6 1

USE OF AN OPTICAL METHOD TO ORIENT BENZENE CRYSTALS

* * *

Frank A. Mullens

USE OF AN OPTICAL METHOD TO

ORIENT BENZENE CRYSTALS

by

Frank A. Mullens

This work is accepted as fulfilling

the thesis requirements for the degree of

MASTER OF SCIENCE

IN

PHYSICS

from the

United States Naval Postgraduate School

ABSTRACT

An experimental investigation was conducted to determine the orientation of the benzene crystal prior to performing ultrasonic absorption measurements. This investigation showed that it was possible, using optical means, to orient the crystal accurately.

The isochromatic curves characteristic of a biaxial crystal were made visible by the use of a convergent beam of polarized white light. These isochromatic curves made it possible to locate the γ, β, and α axes of the triaxial ellipsoid, the optic axes, and the optic plane in samples of the order of two centimeters thick. It was then necessary to determine the relationship between the a, b, and c axes of the crystal and the direction of the α, β, and γ indices of refraction in the benzene crystal. This was accomplished and determined to be as follows: α -a, β -c, and γ -b.

With these determinations, it would be possible to make ultrasonic absorption measurements along any one of the three crystal axes.

The writer wishes to express his appreciation for the assistance and encouragement given him by Professor O. B. Wilson and Mr. Moeller, of the U. S. Naval Postgraduate School.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

CRYSTAL GROWING

Prior attempts to grow large solid benzene crystals proved successful only to a limited degree, and required cumbersome equipment. For this reason a new method was devised not only to produce larger single crystals, but also to eliminate much of the equipment.

By using a bowl shaped pyrex dessicator jar with a lid that could be sealed and with an entry hole for the insertion of a cold finger, it was possible to observe the growth of the crystal from any direction. This bowl was placed in a larger, partially insulated metal tub which was placed down in the opening of the refrigerator.

The pyrex bowl was filled approximately two thirds full with Reagent-grade benzene. The cold finger was inserted through the hole in the cover of the bowl with a rubber stopper seal. The cover joint was sealed to the bowl with No-Naq stopcock grease. In a method similar to that used by Rockman,[4] the liquid benzene was degassed. With cold methyl alcohol circulating through the cold finger, and cold air surrounding the bowl from below, solid benzene crystals formed down from the cold finger tip, and up from the bottom of the bowl. By adjusting the temperature of the refrigerator, the rate of crystal formation could be controlled. With this particular arrangement, the crystals formed on the bottom of the bowl were much larger than those formed on the cold finger. Also, the size of crystal was largely influenced by the rate of growth; faster growth, smaller crystal, etc. It would appear possible to grow benzene crystals without the use of a cold finger, but further steps along this line were not taken.

OPTICAL ANALYSIS OF BENZENE CRYSTAL

Rockman[4] has made some ultrasonic absorption measurements on a benzene crystal. However, there was no attempt made to determine along which crystal axis these measurements were made. Since the velocity of light in anisotropic crystals varies with the direction of propagation, it seems reasonable to expect that the ultrasonic wave velocity and, perhaps, the ultrasonic absorption would also vary with direction. For this reason, it was necessary to determine at least one of the crystal axes so that repeated measurements could be taken along the same direction.

One method widely used to determine crystal axes is the x-ray diffraction method. In this case, with the melting point of benzene around 5.5 degrees Centigrade, the x-ray method would require a very elaborate cooling system for the crystal while it was being irradiated, or the insertion of the whole system in a refrigerator. Therefore, it was decided to use optical means.

For small crystals, the polarizing microscope is generally used for determinations of this type. In order to use the method on the large benzene crystal, certain modifications had to be made.

The optical layout is as shown on page 13. The whole system had to be made small enough to fit down in the refrigerator and yet permit viewing of the optical properties from above. Essentially parallel light, either white or monochromatic, passed through the bottom polaroid plate with the aid of mirrors or prisms, and then through a condensing lens with a very short focal length, strikes the face of the benzene crystal and is divided into two rays, each of which travels through the crystal with a different velocity, and,

usually, in different directions.[1] These two rays are polarized in planes at right angles to one another, and upon passing through a properly oriented analyzer are either passed or blocked out. Solid benzene forms a orthorhombic crystal. It has three mutually perpendicular axes of different lengths.[1] The axes of the triaxial ellipsoid also lie along the crystalline axes of the orthorhombic class crystal. The benzene crystal is therefore a biaxial crystal and possesses two directions which correspond very closely to the optic axes in uniaxial crystals. Quoting from Hartshorne and Stuart,[1] "In general, when a ray of monochromatic light enters a biaxial crystal it is divided into two rays polarized in planes at right angles to one another, but neither of these rays obeys the ordinary laws of refraction; in other words, two extraordinary rays are formed. Passing through any point in the crystal, however, there are three planes at right angles to one another, each of which is characterised by the fact that one of the two rays which can travel in any direction in it has a constant refraction index. These three planes are defined by three mutually perpendicular axes which are, respectively, the vibration directions of rays having the maximum, the minimum, and a particular intermediate refractive index. In an orthorhombic crystal these axes run in the same directions as the crystallographic axes." Since this is the case, it should be possible by optical means, to determine the three crystallographic axes of the benzene crystal. When a crystal of this type is viewed in the system described above, isochromatic curves may appear, their shape depending on the orientation of the crystal. This orientation is quite important, because unless the position of the crystal is such as to show the optic axes, the isochromatic curves are unobservable.

Although many optical studies of crystals have been described in the literature, none was found which had been made on large single crystals of benzene. For this reason, it was necessary to investigate by experiment the best means for crystal preparation, cutting, optical viewing, and orientation.

PREPARATION OF CRYSTAL FOR OPTICAL ORIENTATION

When the solid benzene formed in the pyrex bowl, as was mentioned in the early part of this report, it was a mass of individual crystals. Prior methods of separating each individual crystal from the entire mass by cutting with a hack saw, as done by Rockman in his experiments with benzene were both difficult and wasteful. Wasteful, in that many individual crystals were destroyed by the cut, and difficult in that the saw had to be reheated quite often in order to keep it from freezing to the benzene. It was found that by slightly raising the temperature of the solid mass of benzene, the individual crystals could then be broken apart by hand.

For the initial analysis of the crystal, it was not necessary to have perfectly parallel faces on the crystal, so that careful facing by hand held tools was all that was necessary. One difficulty encountered with the facing of the crystal was the sublimation of the benzene. As quickly as a face was prepared, it became opaque due to this sublimation. Therefore various means were tested to keep the faces optically transparent. The method found best was to press a glass microscope slide, at room temperature, against the face of the crystal, and thus allow it first to melt some of the benzene and then to freeze to the crystal. With one of these flats on each of the approximately parallel faces, the crystal was inserted in the light bean of the analyzing apparatus to see if the isochromatic curves were visible.

As a rule, inspection of the sample with this first facing gave no curves, or at least none were visible. However, by judicious

rotation of the polaroid analyzer and the sample, it was possible to locate the orientations of the crystal which gave maximum extinction of light. Since the light rays passing through the crystal were broken into two rays vibrating in planes perpendicular to each other, the positions of maximum extinction located these planes. At maximum extinction, one of the rays was being extinguished by the analyzer. This meant that its direction of vibration was perpendicular to that of the analyzer. The direction of these two perpendicular planes, was marked on the optical flat with a grease pencil. If then, two new parallel faces were made on the crystal parallel to one of the axes marked on the flat, and the same procedure followed as before, the new perpendicular planes on these new faces were located. Repeating this procedure once again, if necessary, and inserting the crystal in the conoscope, one or possibly both optical axes of the crystal could be seen.

By adjusting the crystal until both of the optic axes were visible, it was possible to see the location of one crystallographic axis by the shape of the isochromatic curves. This axis appeared on a line joining the two optic axes and halfway between them. Since the optical properties of benzene indicate that it has large positive birefringence[1], the axis appearing between the two optic axes is the δ axis of the triaxial ellipsoid.[3] Also, the plane formed by the two optic axes contains the δ and β axes. Thus, the three mutually perpendicular axes of the triaxial ellipsoid were approximately located. At this point, before cutting a speciman from the sample crystal, it was necessary to make the opposite faces of the crystal exactly parallel so that the crystal axis under study would be

parallel to the axis of the conoscope. The optical layout, as pictured on page 13 was designed so that a cutter tube, which will be described later, could be raised and lowered along the axis of the system. A metal facing plate was designed to fit snugly in the top of the cutter tube, so that, when the tube was raised, this plate would melt a face on the crystal that was perpendicular to the axis of the system. Then, by rotating the goniometer 180 degrees and making another face in the same manner as before, a pair of accurately parallel faces was prepared. A check on the orientation of the axis was made, and, if not in alignment, the orientation was changed appropriately and the facing was repeated.

After assuring that the δ axis and the normals to the faces were aligned with the optical system and that the angular position of the optic plane was known, the sample was ready for cutting. The cutter tube consists of a nickel cylinder with a filament wire secured around one end. As the cutter tube was raised and a small amount of current supplied to the filament wire, the heat from the wire melted a cylindrical specimen from the sample. The facing plate that was used to make parallel faces on the sample, was removed for this operation. Picture 13 shows the tube with facing plate in place, and picture shows the cutter tube ready for the cutting operation. Some caution had to be exercised during the cutting operation to make certain that the temperature of the filament wire did not approach the flash point of benzene.

The goniometer arrangement permits the choice of any desired crystal axis as the axis for the cylindrical specimen.

RELATIONSHIP BETWEEN THE TRIAXIAL ELLIPSOID AXES AND THE UNIT CELL AXES

There was available in the literature the knowledge that the b crystalline axis in the orthorhombic crystal class corresponds to the direction of vibration having the slowest velocity (greatest index). However, it was necessary to determine by some analysis which of the other two crystalline axes correspond to the α and β indices. The method used here was to construct a scale model of the unit cell for study. Data for this arose from x-ray methods.

The cell dimensions at -3 degrees Centigrade are a = 7.460; b = 9.666; and c = 7.034 A.[2] The individual molecule is accurately planar and the normal to its plane makes angles of $44^{\circ}49'$, $77^{\circ}04'$, and $48^{\circ}04'$ with the a, b, and c axes respectively. Pages 16, 17 and 18 show this cell, looking along each of the <u>three</u> axes. On studying this unit cell, it was possible to determine the relationships between the α, β, and γ axes of the ellipsoid; and the a, b, and c axes of the cell. The γ axis indicates the electric vector vibration direction which has the greatest index of refraction, the α direction the least, and the β direction the intermediate index of refraction.

The greatest interaction with the benzene molecule occurs when the vibration direction of the light is parallel to the plane of the molecule.[1] From examination of the unit cell, this occurs along the b axis. This means that the γ axis corresponds to the b axis of the unit cell. In similar manner it was seen that the β axis corresponds to the c axis, and the α axis to the a axis. Knowing this relationship, the optic plane, as seen in the benzene crystal, is the b-c plane of the unit cell. Thus, with this knowledge and with the optical apparatus as shown on page 13, it was possible to orient the sample faces

relative to the crystallographic axes so that wave velocity and the absorption measurements may be made in known directions.

METHODS OF MOUNTING SPECIMEN IN HOLDER AND POLISHING THE FACES

After obtaining a cylindrical speciman, with its axis parallel to one of the desired axes, it was ready for insertion in the specimen holder. This holder is a brass ring constructed so that its ends are parallel and the inner diameter is just large enough to allow the cylindrical specimen to slide through. The specimen was then frozen to the ring by dropping liquid benzene between it and the cold ring, and allowing it to freeze. A brass ring is used because as the specimen was faced with fine emery paper, it was possible to make its faces plane parallel with those of the ring. The fact that the benzene is soft, and, worse, has a high vapor pressure, prohibits the use of conventional grinding techniques. The final polishing was done using bond paper in place of the emery paper.

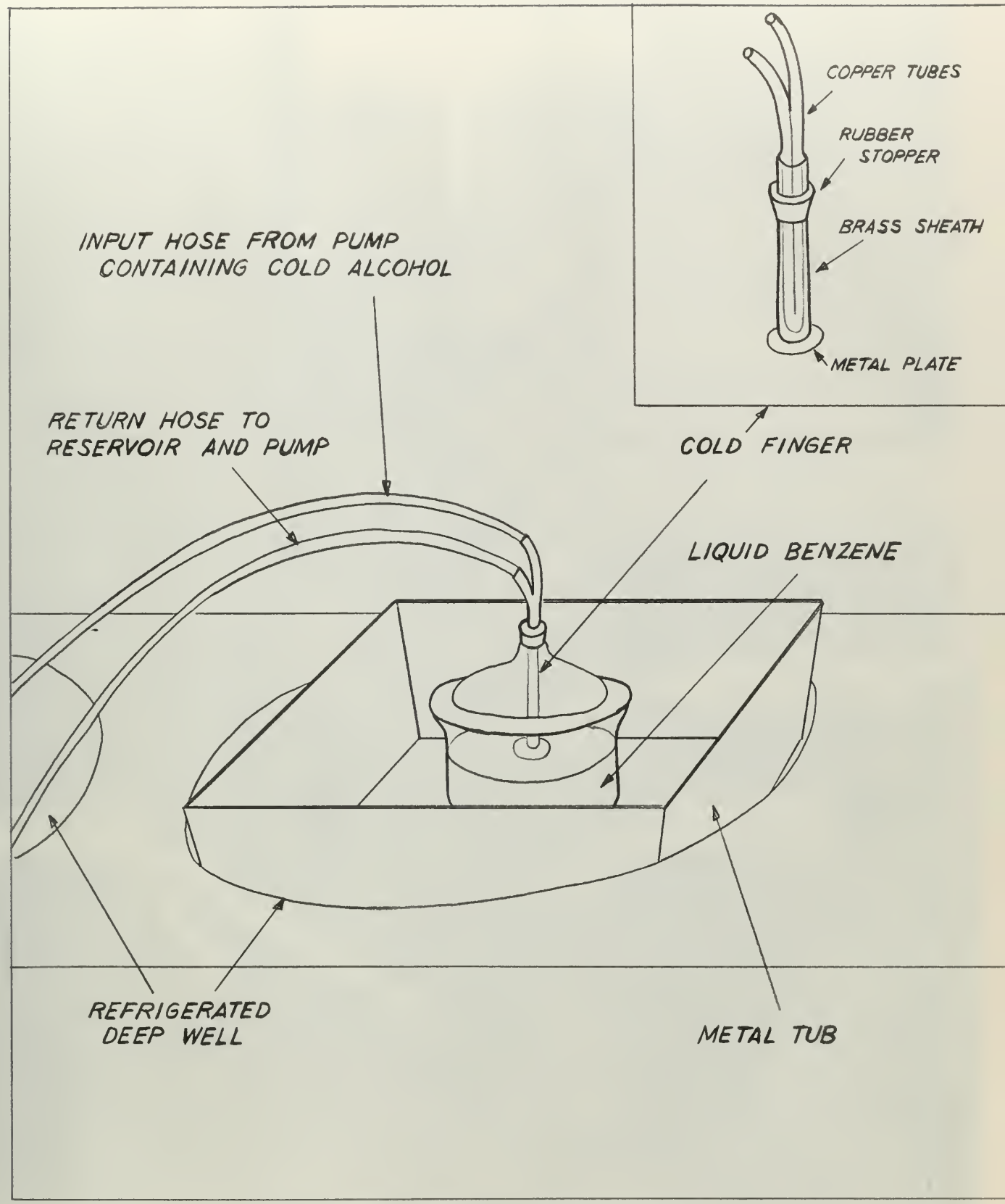
METHOD OF SEALING FACES, AND MOUNTING OF QUARTZ TRANSDUCER

Once the specimen was prepared, it was imperative that some means of preventing sublimation be provided.

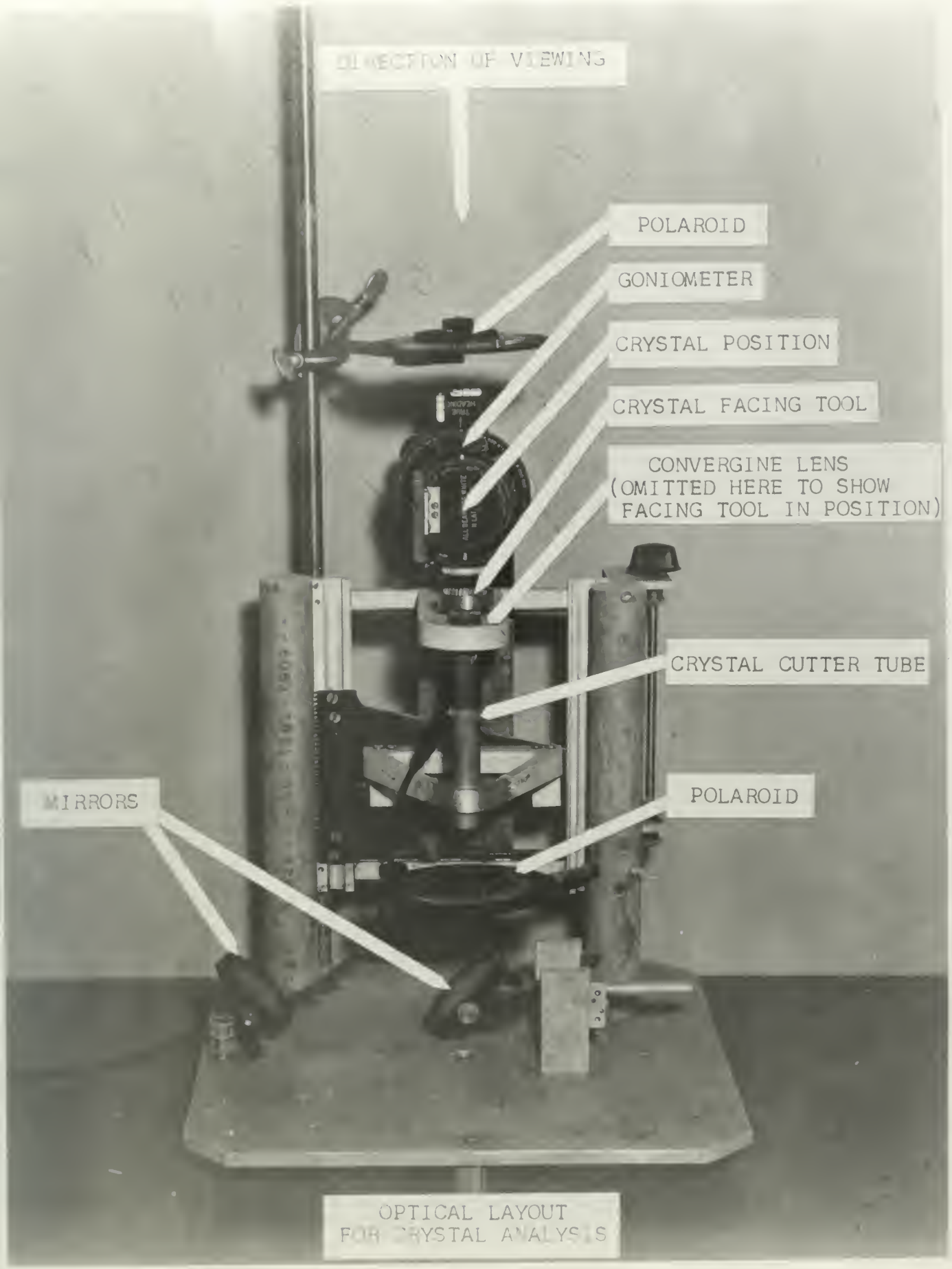
Two methods were used to seal the faces of the sample. On one face, a thin film of gold foil, approximately .0005" thick was attached with the aid of gylcerine. A drop of gylcerine was placed on the specimen face, then the gold foil was spread over the face and any excess gylcerine was removed by using a spreader. In this way, all the air was removed from contact with the crystal face. The other face of the specimen was sealed by placing an aluminum cover over it, and screwing this cover to the brass ring. This did not provide for an airtight seal, however, the tendency for sublimation to occur was greatly reduced.

A quartz transducer was used to provide a mechanical pulse to the specimen. An electrical pulse was sent to the transducer, which converted this electrical pulse into a mechanical pulse, which was then sent through the specimen. The transducer was fastened to the gold foil face of the specimen by means of gylcerine as before. Care had to be taken so as to make the bond between the gold foil and the transducer just as thin as possible. At this point the specimen was ready for mounting in the test equipment. The method of mounting in the test equipment, with the exception of the brass ring as described earlier, was essentially the same as that used by Rockman[4] in his experiment.

Although some ultrasonic pulse measurements were made using this method of preparing the sample faces, none were carried out on samples of known crystallographic orientation.



CRYSTAL GROWING APPARATUS



OPTICAL LAYOUT
FOR CRYSTAL ANALYSIS

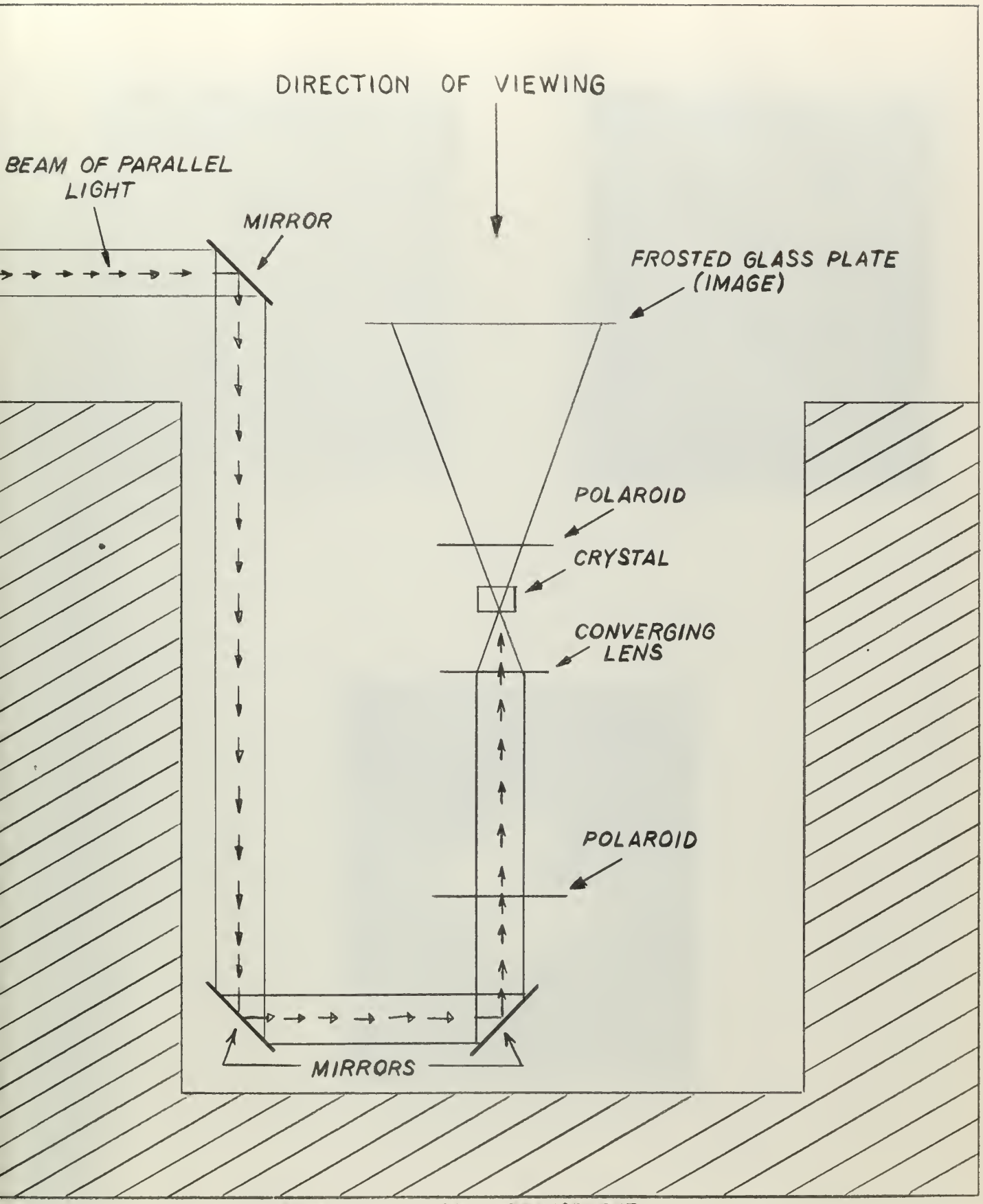
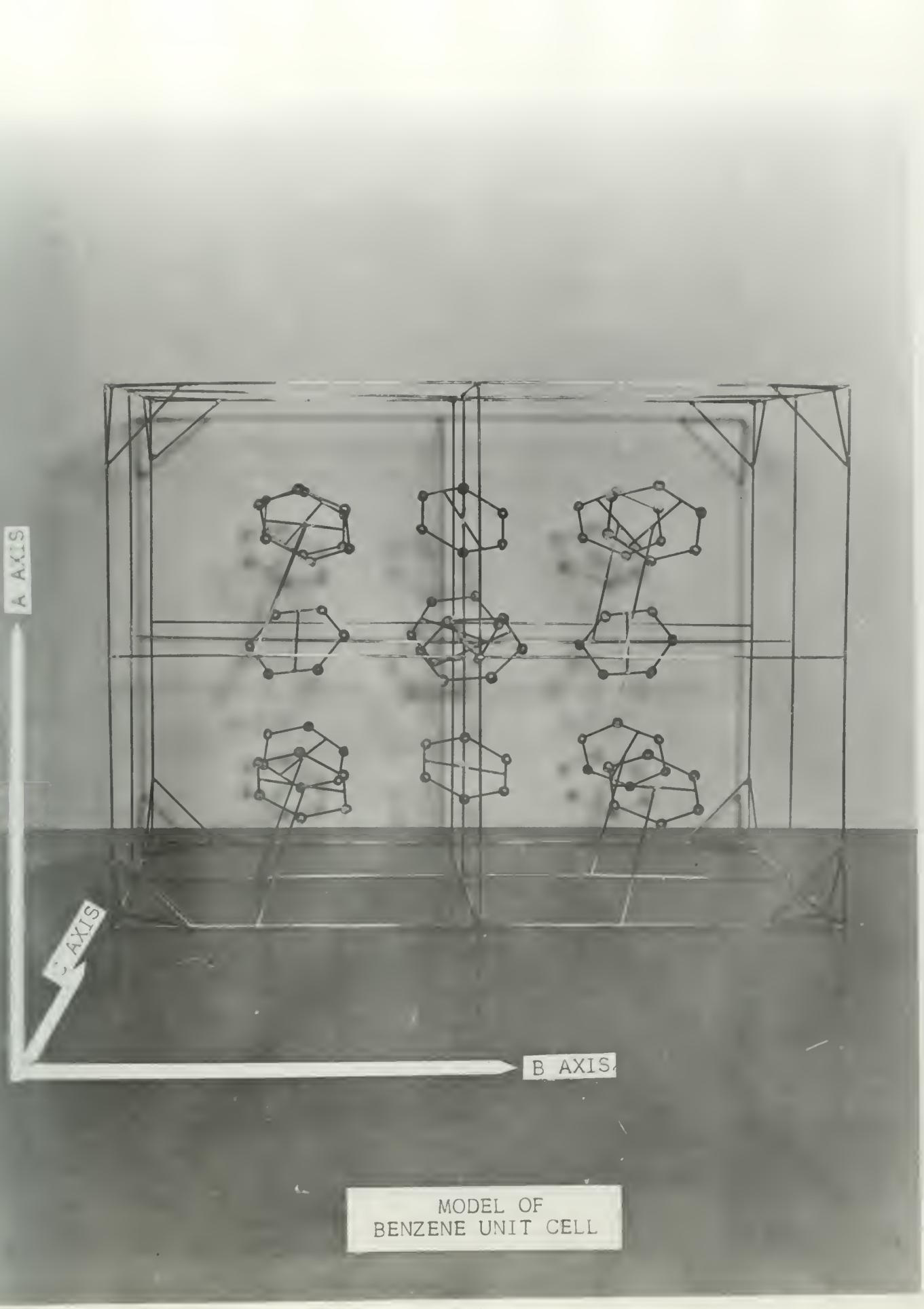


DIAGRAM OF OPTICAL ARRANGEMENT

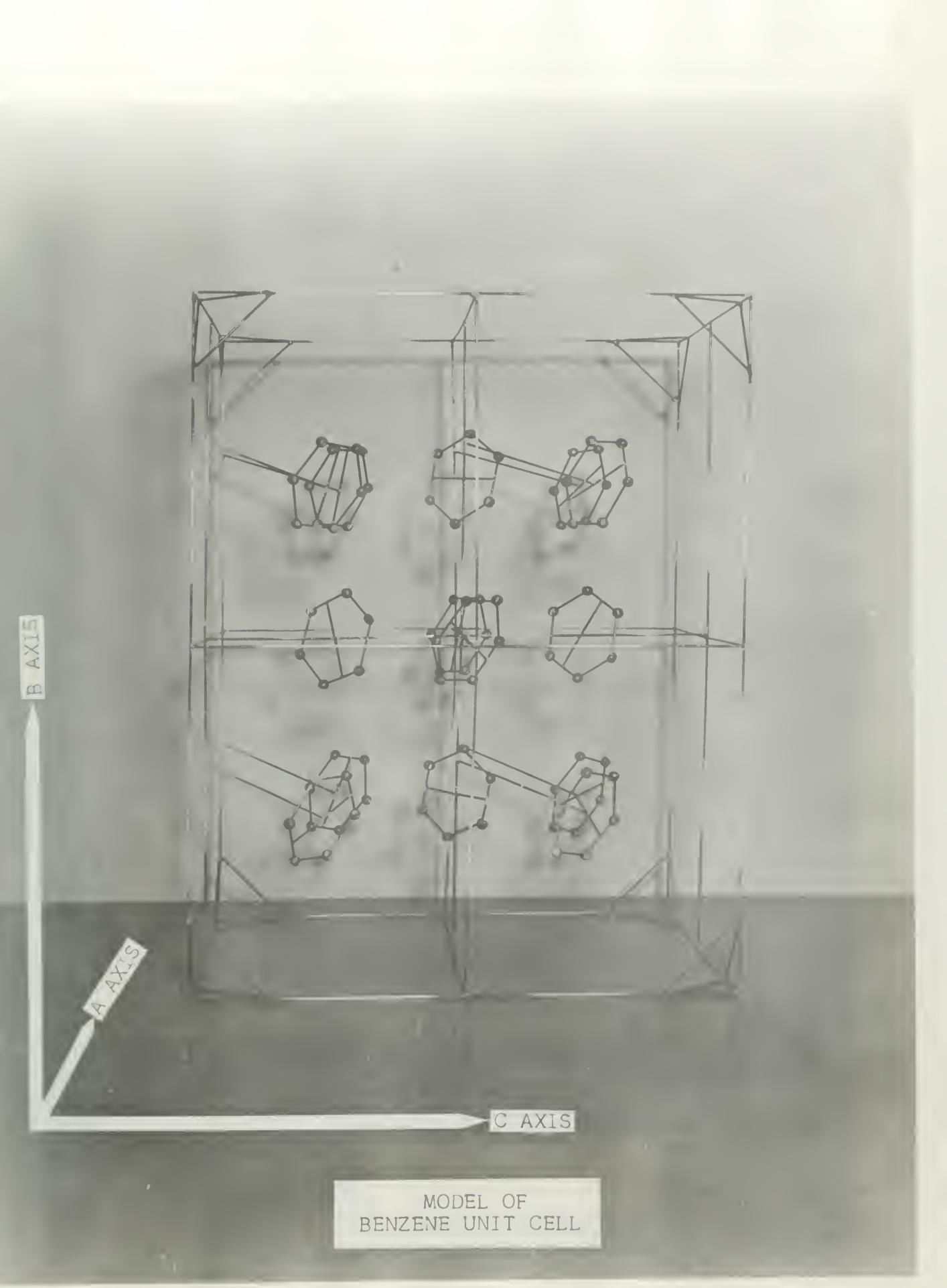
Isochromatic Curves
Around The [illegible] Axis

Isochromatic Curves
Around an Optic Axis

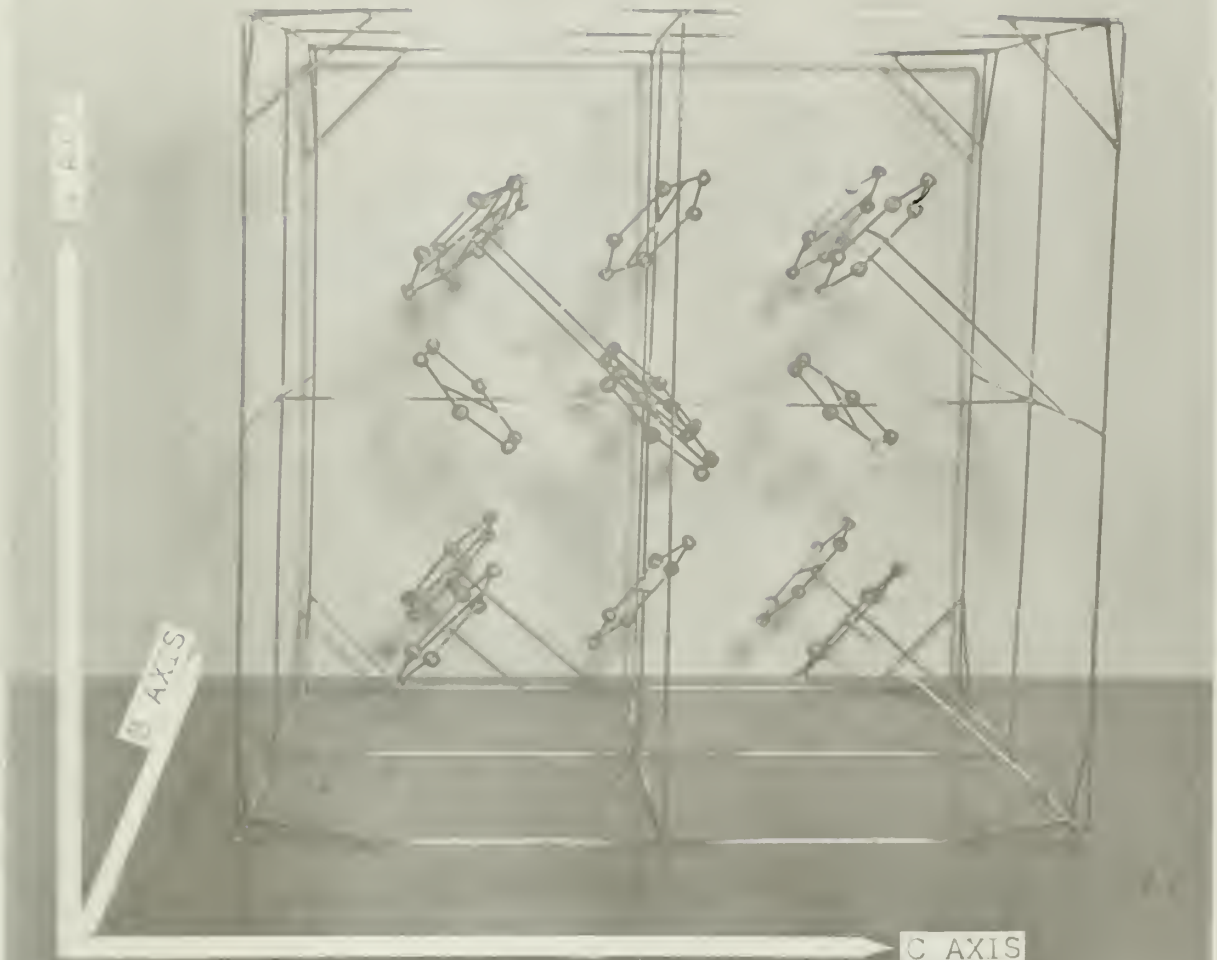
Photograph showing [illegible]
optic axes with the black
brush between them.



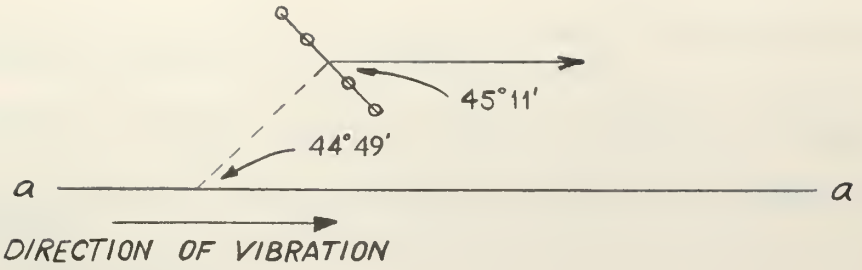
MODEL OF
BENZENE UNIT CELL

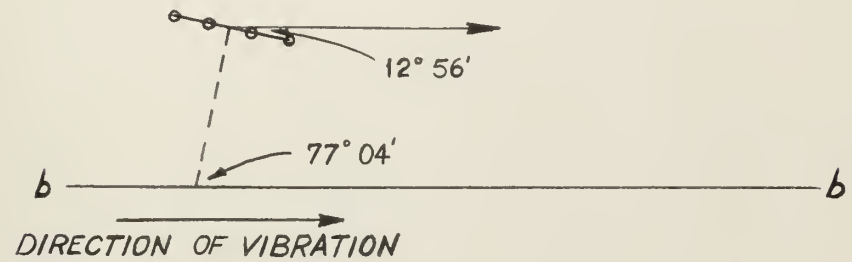


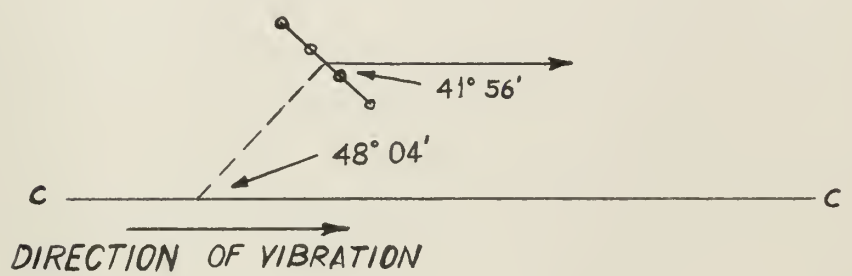
MODEL OF
BENZENE UNIT CELL



MODEL OF
BENZENE UNIT CELL







γ = Axis with Greatest Index of Refraction = b

α = Axis with Least Index of Refraction = a

β = Axis with Intermediate Index of Refraction = c

BIBLIOGRAPHY

1. Hartshorne and Stuart, Crystals and the Polarizing Microscope, Edward Arnold and Co., 2d Edition, 1950.

2. Reviews of Modern Physics, Volume 30, Number 1, January 1958.

3. W. F. de Jong, General Crystallography, W. H. Freeman and Co., 1959.

4. Rockman, Thesis.